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PRINTING INK BINDER  
[Insatsu Inki Yo Baida]

Kenji Yamashita

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Inventors : Kenji Yamashita  
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## PRINTING INK BINDER

Summary

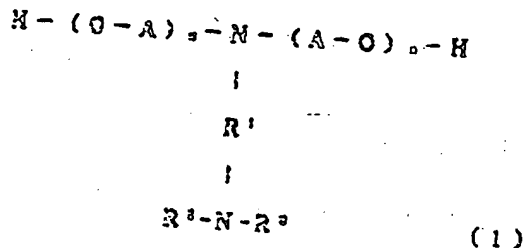
Objective: To provide a printing ink binder with the following characteristics: In a polyurethane resin-type printing ink (especially a special gravure ink) binder, the adhesive strength with a polyolefin film, which has heretofore been questionable, is improved, and the viscosity stability of a case where it is used in a double-liquid ink is also improved.

Constitution: A printing ink binder which consists of a solvent solution which contains a polyurethane resin which possesses a tertiary amino group in its side chain and which is obtained by reacting (a) a diol (e.g., N,N-dimethylaminopropylamine-ethylene oxide 2 mole adduct, etc.), (b) a high-molecular-weight diol (e.g., polybutylene adipate diol, etc.), (c) an organic diisocyanate (e.g., IPDI, etc.), and (d) a chain extending agent (e.g., isophoronediamine) as well as (optional) (e) a polymerization terminator (e.g., di-n-butylamine, etc.).

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<sup>1</sup>Numbers in the margin indicate pagination in the foreign text

1. A printing ink binder with the following characteristics:  
In a printing ink binder which consists of a polyurethane resin, said polyurethane resin is a polyurethane resin which possesses a dialkylamino group in its molecule side chain and which is obtained by reacting (a) a diol represented by the following general formula: [chemical 1]:



(wherein A is an alkylene group containing 2-4 carbon atoms; R<sup>1</sup> is an alkylene group containing 1-5 carbon atoms; R<sup>2</sup> and R<sup>3</sup> are alkyl groups containing 1-5 carbon atoms; m and n are 0 or positive integers which satisfy the relationship of (m + n) = 1-10), (b) a high-molecular-weight diol, (c) an organic diisocyanate, and (d) a chain extending agent as well as (optional) (e) a polymerization terminator.

2. The binder specified in Claim 1 wherein the tertiary amine value of the total dialkylamino groups located in the molecule side chain of said polyurethane resin is 1-30.

## Detailed explanation of the invention

[0001]

(Industrial application fields of the invention)

The present invention concerns a printing ink binder.

[0002]

(Prior art of the invention)

Concrete examples of polyurethane resins used in conventionally-known plastic film printing ink binders include one which possesses an alkyl group at the molecule terminal (Japanese Patent Application Publication No. Kokai Sho 54[1979]-36960), one which possesses a hydroxyl group at the molecule terminal (Japanese Patent Disclosure No. Tokkai Sho 61[1986]-66769), etc. The adhesive strengths of printing ink binders which use them, however, are insufficient when they are applied to a polypropylene film, polyethylene film, etc. In order to improve the adhesive strengths with these polyolefin films, (1) a polyurethane resin which possesses a special tertiary amino group in the polyurethane molecule principal chain (e.g., Japanese Patent Application Publication No. Kokai Hei 1[1989]-37427) and (2) one which possesses an amino group at the molecule terminal (Japanese Patent Disclosure No. Tokkai Sho 62[1987]-292873) have heretofore been proposed.

[0003]

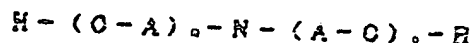
(Problems to be solved by the invention)

The adhesive strength of (1) with the polyolefin film, however, is still insufficient. The viscosity stability of (2) is questionable in a case where a double-liquid ink is prepared.

[0004]

(Mechanism for solving the problems)

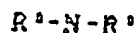
The present inventors compiled exhaustive research in order to solve the aforementioned problems, and as a result, the present invention has been completed. Put succinctly, the present invention concerns a printing ink binder with the following characteristics: In a printing ink binder which consists of a polyurethane resin, said polyurethane resin is a polyurethane resin with a tertiary amine value of 1-30 which possesses a dialkylamino group in its molecule side chain and which is obtained by reacting (a) a diol represented by the following general formula: [chemical 2]:



|

R<sup>2</sup>

|



(1)

(wherein A is an alkylene group containing 2-4 carbon atoms; R<sup>1</sup> is an alkylene group containing 1-5 carbon atoms; R<sup>2</sup> and R<sup>3</sup> are alkyl groups containing 1-5 carbon atoms; m and n are 0 or positive integers which satisfy the relationship of (m + n) = 1-10), (b) a

high-molecular-weight diol, (c) an organic diisocyanate, and (d) a chain extending agent as well as (optional) (e) a polymerization terminator.

[0005]

Alkylene oxide (e.g., alkylene oxides containing 2-4 carbon atoms such as ethylene oxide propylene oxide, butylene oxide, etc.) adducts of N,N-dialkylaminoalkylamines as well as mixtures consisting of two or more types of these polymers can be employed as diols corresponding to component (a) of the present invention. Concrete examples of these diols (a) include an N,N-dimethylaminoethylamine-ethylene oxide 1-10 mole adduct, N,N-dimethylaminoethylamine-propylene oxide 1-10 mole adduct, N,N-dimethylaminopropylamine-ethylene oxide 1-10 mole adduct, N,N-dimethylaminopropylamine-propylene oxide 1-10 mole adduct, N,N-diethylaminoethylamine-ethylene oxide, N,N-diethylaminoethylamine-propylene oxide 1-10 mole adduct, N,N-diethylaminopropylamine-ethylene oxide 1-10 mole adduct, N,N-diethylaminopropylamine-propylene oxide 1-10 mole adduct, N,N-dibutylaminoethylamine-ethylene oxide 1-10 mole adduct, N,N-dibutylaminoethylamine-propylene oxide 1-10 mole adduct, N,N-dibutylaminopropylamine-ethylene oxide 1-10 mole adduct, N,N-dibutylaminopropylamine-propylene oxide 1-10 mole adduct, and mixtures of two or more types of these adducts.

[0006]

Generally speaking, the average molecular weight (which is based on the hydroxyl value measurement) of said diol (a) is 700 or

lower, preferably 500 or lower. If the average molecular weight exceeds 700, the oil-resistance of the resulting printed matter deteriorates.

[0007]

Polyether diols and polyester diols can be employed as the high-molecular-weight diol (b) of the present invention. Concrete examples of said polyether diols include (1) low-molecular-weight diol-alkylene oxide adducts, (2) [decyclized] (co)polymers of alkylene oxides and/or cyclo ethers, etc. /3

[0008]

Concrete examples of low-molecular-weight diols corresponding to (1) include aliphatic low-molecular-weight diols (e.g., ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4- and 1,3-butane diol, neopentyl glycol, pentane diol, 3-methylpentane diol, 1,6-hexane diol, 1,8-octamethylene diol, alkyldialkanolamine, etc.), low-molecular-weight diols which possess cyclic groups (e.g., ones mentioned in Japanese Patent Application Publication No. Kokai Hei 1[1989]-1474 such as bis(hydroxymethyl)cyclohexane, m- and p-xylylene glycols, bis(hydroxyethyl[ ])benzene, 1,4-bis(2-hydroxyethoxy)benzene, 4,4'-bis(2-[hy]droxyethoxy)diphenylpropane (bisphenol A ethylene oxide adduct), etc.), and mixtures of two or more types of these compounds.

[0009]

Concrete examples of alkylene oxides corresponding to (1) include alkylene oxides containing 2-4 carbon atoms (e.g., ethylene



oxide, propylene oxide, 1,2-, 2,3-, and 1,3-butylene oxides, etc.).

[0010]

Concrete examples of [decyclized] (co)polymers corresponding to (2) include products obtained by decyclizing and [homo]polymerizing or decyclizing and copolymerizing (block and/or random) the alkylene oxides and/or cyclo ethers mentioned in (1) (e.g., tetrahydrofuran, etc.).

↑ MW

[0011]

Concrete examples of polyether diols include polyethylene glycol, polypropylene glycol, polyoxyethylene-polyoxypropylene diol (block and/or random), polytetramethylene ether glycol, polytetramethylene ether-polyoxyethylene diol (block and/or random), polytetramethylene ether-polyoxypropylene diol (block and/or random), polyhexamethylene ether glycol, polyoctamethylene ether glycol, and mixtures of two or more types of these polymers.

[0012]

Concrete examples of polyester diols include (3) condensed polyester diols obtained by reacting low-molecular-weight diols and/or polyether diols with molecular weights of 1,000 or lower with dicarboxylic acids and/or hydroxymonocarboxylic acids, (4) polylactone diols obtained by decyclizing and polymerizing lactones, etc.

↑ MW

[0013]

Ones identical to those mentioned in (1) can be employed as the low-molecular-weight diols employed in (3). Concrete examples of polyether diols with molecular weights of 1,000 or lower

employed in (3) include some of the aforementioned polyether diols with molecular weights of 1,000 or lower such as polyethylene glycol, polytetramethylene ether glycol, polytetramethylene ether glycol, polypropylene glycol, triethylene glycol, and mixtures of two or more types of these polymers.

[0014]

Concrete examples of dicarboxylic acids employed in (3) include aliphatic dicarboxylic acids (e.g., succinic acid, adipic acid, sebacic acid, glutaric acid, azelaic acid, maleic acid, fumaric acid, etc.), aromatic dicarboxylic acids (e.g., terephthalic acid, isophthalic acid, etc.), and mixtures of two or more types of these acids. Concrete examples of lactones corresponding to (4) include  $\epsilon$ -caprolactone,  $\delta$ -valerolactone, etc.

[0015]

Concrete examples of these polyester diols include polyethylene adipate, polybutylene adipate, polyhexamethylene adipate, polyneopentyl adipate, poly-3-methylpentane adipate, polyethylene propylene adipate, polyethylene butylene adipate, polybutylene hexamethylene adipate, polydiethylene adipate, poly(polytetramethylene ether) adipate, polyethylene azelate, polybutylene sebacate, polycaprolactone diol, polyvalerolactone diol, polycarbonate diol, and mixtures of two or more types of these polymers.

[0016]

In a case where these high-molecular-weight diols (b) are employed, it is generally desirable that the polyester

diol/polyether diol ratio be controlled within a range of 100/0-50/50 (weight ratio), preferably 100/0-70/30 (weight ratio). In a case where the ratio of the polyester diol is less than [50%], the oil resistance of the printed matter deteriorates. Generally speaking, the average molecular weights of these high-molecular-weight diols (b) (based on the hydroxyl value measurement) are 500-5,000, preferably 700-4,000.

[0017]

Concrete examples of organic diisocyanates which can be employed as component (c) of the present invention include alicyclic diisocyanates containing 2-12 carbon atoms (excluding the carbon atoms of CO groups), alicyclic diisocyanates containing 4-15 carbon atoms, aromatic and aliphatic diisocyanates containing 8-12 carbon atoms, aromatic diisocyanates containing 6-20 carbon atoms, and modified derivatives of these organic diisocyanates (e.g., modified products containing carbodiimido groups, urethodione group, urethoimine group, urea group, bureto group, and/or isocyanato groups).

[0018]

Concrete examples of such organic diisocyanates include aliphatic diisocyanates (e.g., ethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate (HDI), dodecamethylene diisocyanate, 1,6-11-undecane triisocyanate, 2,2,4-trimethylhexane diisocyanate, lysine diisocyanate, 2,6-diisocyanatomethylcaproate, bis(2-isocyanatoethyl) fumarate, bis(2-isocyanatoethyl) carbonate, 2-isocyanatoethyl-2,6-diisocyanate

hexanoate, etc.), alicyclic diisocyanates (e.g., isophorone diisocyanate (IPDI), dicyclohexylmethane diisocyanate (hydrogenated MDI), cyclohexylene diisocyanate, methylcyclohexylene diisocyanate (hydrogenated TDI), bis(2-isocyanatoethyl)-4-cyclohexene-1,2-dicarboxylate, etc.), aromatic and aliphatic diisocyanates, (e.g., xylylene diisocyanate, tetramethyl xylylene diisocyanate, diethylbenzene diisocyanate, etc.), aromatic diisocyanates /4 (e.g., toluylene diisocyanate (TDI), crude TDI, diphenylmethane diisocyanate (MDI), polyphenylmethane polyisocyanate (crude MDI), modified MDIs (e.g., carbodiimide-modified diisocyanate, etc.), and mixtures of two or more types of these compounds. Of these examples, aliphatic diisocyanates, alicyclic diisocyanates, and aromatic and aliphatic diisocyanates are especially desirable.

[0019]

Low-molecular-weight diols or diamines with molecular weights of less than 500 are employed as the chain extending agent (d) of the present invention. Concrete examples of such low-molecular-weight diols include diols identical to those used as feed materials for manufacturing the aforementioned polyester diols, their alkylene oxide lower mole adducts (molecular weights: Lower than 500), etc.

[0020]

Concrete examples of diamines include aliphatic diamines (e.g., ethylenediamine, hexamethylenediamine, 1,2-propylenediamine, 2,2,4-trimethylhexamethylenediamine, 2-hydroxyethylethylenediamine, di-2-hydroxyethylethylenediamine, etc.), alicyclic diamines (e.g.,

isophoronediamine, 4,4'-dicyclohexylmethanediamine, isopropylidenedicyclohexyl-4,4'-diamine, 1,4-diaminodiphenylmethane, etc.), aromatic and aliphatic diamines (e.g., xylenediamine, etc.), hydrazine, dihydrazides (e.g., adipic dihydrazide, etc.), and mixtures of two or more types of these substances. Of these, low-molecular-weight diols, alicyclic diamines, and their combinations are especially desirable as said component (b).

[0021]

If necessary, furthermore, polymerization terminators may be employed as component (e). Concrete examples of substances which can be employed as said polymerization terminator (e) include monovalent alcohols (e.g., methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, etc.), monoamines (e.g., monoethylamine, n-propylamine, n-butylamine, di-n-propylamine, di-n-butylamine, etc.), hydroxylmonoamines (e.g., monoethanolamine, diethanolamine, etc.).

[0022]

As far as the present invention is concerned, it is desirable that the quantity of the diol (a) is selected in such a way that the diol (a)/polymer diol (b) weight ratio will usually be controlled within a range of 0.5/95.5-50/50, preferably 1/99-40/60. In a case where the quantity of the diol (a) is larger than that of the high-molecular-weight diol (b), the film strength of the polyurethane resin becomes hard [sic: Discrepancy], and the adhesive strength of the resulting ink with a film deteriorates.

[0023]

Concrete examples of methods for manufacturing the polyurethane resin of the present invention include (1) the one shot method, wherein the diol (a), high-molecular-weight diol (b), organic diisocyanate (c), and the chain extending agent (d) (as well as the polymerization terminator (e), if necessary) are reacted all at once and (2) the prepolymer method wherein a urethane prepolymer which possesses isocyanato groups at both terminals is first prepared from the diol (a), high-molecular-weight diol (b), and an excess of the organic diisocyanate (c) and wherein said prepolymer is reacted with the chain extending agent (d) (as well as the polymerization terminator (e), if necessary). The prepolymer method (2) is the more desirable in consideration of the production efficiency.

[0024]

In a case where the aforementioned urethane prepolymer is manufactured in the prepolymer method (2), it is generally desirable that the equivalent ratio between the isocyanato groups of the organic diisocyanate (c) and the combined hydroxyl groups of the diol (a) and the high-molecular-weight diol (b) be controlled within a range of 1.1/1.0-5.0/1.0, preferably 1.2/1.0-3.0/1.0. Moreover, it is desirable that the combined quantities of the chain extending agent (d) and polymerization terminator (e) be virtually equivalent to the isocyanato groups of the prepolymer. For example, it is desirable that the combined quantities of the active hydrogen groups of the chain extending agent (d) and polymerization

terminator (e) with respect to 1 equivalent of the isocyanato groups of the prepolymer be 0.91-1.05 equivalents, preferably 0.96-1.02 equivalents.

[0025]

In a case where the molecule terminal of the polyurethane resin is converted into an amino group in the prepolymer method, an excess of diamine is used with respect to the isocyanato groups of the prepolymer. For example, it is generally desirable that the quantity of the diamine with respect to 1 equivalent of the isocyanato groups of the prepolymer be 1.02-1.3 equivalents, preferably 1.05-1.2 equivalents. If necessary, furthermore, the polymerization terminator (e) can be used in combination in this case, too.

[0026]

The polyurethane resin of the present invention is manufactured in the presence or absence of solvents. Concrete examples of applicable solvents include ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, etc.), esters (e.g., ethyl acetate, propyl acetate, butyl acetate, etc.), ethers (e.g., tetrahydrofuran, etc.), aromatic hydrocarbons (e.g., toluene, xylene, etc.), alcohols (e.g., methanol, ethanol, isopropyl alcohol, etc.), polyvalent alcohol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, etc.), amides (e.g., dimethylformamide, etc.), sulfoxides (e.g., dimethyl sulfoxide, etc.), and mixed solvents consisting of two or more types of these solvents. Of these, acetone, methyl ethyl ketone,

methyl isobutyl ketone, ethyl acetate, propyl acetate, butyl acetate, tetrahydrofuran, toluene, xylene, methanol, ethanol, isopropyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and mixed solvents consisting of two or more types of the foregoing examples are especially desirable. The quantity of the solvent is selected in such a way that the polyurethane resin/solvent weight ratio will be controlled within a range of 100/0-10/90, preferably 80/20-20/80.

[0027]

The aforementioned polyurethane resin may be employed alone as a resin that constitutes the printing ink binder of the present invention. If necessary, furthermore, it may be used in combination with conventionally-known resins which have heretofore been employed as printing ink binders. Concrete examples of applicable optional resins include polyamides, nitro cellulose, polyacrylates, polyvinyl chloride, vinyl chloride-vinyl acetate /5 copolymer, styrene-butadiene rubber, epoxy resin, rosin resin, etc. In cases where they are used, it is desirable that the quantities of the optional resins with respect to the solid content of the binder be no higher than 50 wt%.

[0028]

Generally speaking, the printing ink binder of the present invention is obtained by solubilizing a resin component which contains said polyurethane resin in the aforementioned solvent. Generally speaking, it is desirable that the resin concentration (weight standard) in the binder of the present invention be 10-



100%, preferably 20-80%. Generally speaking, it is desirable that its viscosity be 50-500,000 cps/20°C, preferably 100-100,000 cps/20°C. Generally speaking, the weight-based average molecular weight of said polyurethane resin is 5,000-100,000, preferably 8,000-80,000.

[0029]

Generally speaking, the tertiary amine value of the side chain dialkylamino group of said polyurethane resin is 0.5-50, preferably 1-30. In a case where the tertiary amine value is lower than 0.5, the adhesive strength is inferior. In a case where it exceeds 50, the water resistance deteriorates.

[0030]

The printing ink binder of the present invention exhibits especially desirable performances as a special gravure ink binder. Concrete examples of application objects include polyester resins, nylon films, polypropylene films, polyethylene films, etc.

[0031]

The printing ink binder of the present invention can be used according to procedures identical to those for conventionally-known ink binders. In other words, a pigment and optional additives (e.g., pigment dispersants, etc.) are added to the binder of the present invention, and after the contents have subsequently been kneaded by using an ordinary ink production apparatus (e.g., ball mill, etc.), a printing ink is obtained.

[0032]

The following is an example of the composition of a printing

ink which contains the ink binder of the present invention ("% signifies "wt%"):

[0033]

Binder of the present invention (solid content):	10-30%;
Pigment:	5-40%;
Solvent (including the solvent in the binder):	40-80%.
Additives:	some

[0034]

In a case where the binder of the present invention is used, it may be used in a single-liquid printing ink. It is also possible to prepare a double-liquid printing ink by using it in combination with a polyisocyanate curing agent. Concrete examples of polyisocyanate curing agents hereby used include an adduct derived from 1 mole of trimethylolpropane and 3 mole of 1,6-hexamethylene diisocyanate, toluylene diisocyanate, or isophorone diisocyanate, isocyanato group-containing cyclic trimer synthesized by cyclizing and trimerizing the isocyanato groups of 1,6-hexamethylene diisocyanate or isophorone diisocyanate, partially buret reaction product synthesized from 1 mole of water and 3 mole of 1,6-hexamethylene diisocyanate, and mixtures consisting of two or more types of these substances. In a case where a double-liquid printing ink is prepared, it is generally desirable that the concentration of the polyisocyanate curing agent with respect to the ink weight be 0.5-10 wt%.

[0035]

In a case where the binder of the present invention is used

for a special gravure ink, printing procedures identical to the conventionally-known ones can be carried out.

[0036]

(Application examples of the invention)

In the paragraphs to follow, the present invention will be explained in further detail with reference to application examples. It should be noted, however, that the scope of the present invention is in no way restricted to these examples. In subsequent references, "parts" and "%" signify "parts by weight" and "wt%," respectively.

[0037]

Application Example 1

After 228.3 parts of a polybutylene adipate diol with a molecular weight of 2,000, 10.8 parts of an N,N-dimethylaminopropylamine-ethylene oxide 2 mole adduct with a molecular weight of 190, and 50.7 parts of isophorone diisocyanate (abbreviated as "IPDI") had been mixed, the contents were reacted at 100°C over a 3-hour period, and as a result, a urethane prepolymer with an NCO content (%) of 1.64 was obtained. After 500 parts of methyl ethyl ketone (abbreviated as "MEK") had subsequently been added, a homogeneous solution was obtained. Subsequently, a solution which had been obtained by solubilizing 8.7 parts of isophoronediamine and 1.5 parts of di-n-butylamine in 200 parts of isopropyl alcohol (abbreviated as "IPA") was added to

*top page 14  
some NCO / NH<sub>2</sub>  
PP CK  
1 / .91-1.05  
So only  
this one  
only 80*

*28%*

the aforementioned MEK urethane prepolymer solution, After the addition had been completed, the temperature was elevated, and the contents were reacted at 50°C over an 8-hour period. The concentration and viscosity of the resulting polyurethane resin solution were 30% and 1,500 cps/20°C, respectively. The total amine value of this resin was 20, and the tertiary amine value of the side chain dialkylamino group was 10 (each based on the polyurethane resin solid content standard).

[0038]

A printing ink binder with the following composition was prepared by using the resulting polyurethane resin solution as a binder: 100 parts of the polyurethane resin solution, 60 parts of a pigment (rutile titanium oxide), 40 parts of toluene, 10 parts of IPA, and 100 parts of ceramic balls (total: 300 parts).

[0039]

After the aforementioned feed mixture had been charged into a steel can with a content volume of 500 mL, the contents were mixed by using a paint conditioner (Shoner, manufactured by Red Devil Co.), and as a result, printing ink [I] was obtained.

[0040]

#### Application Example 2

After [19]5.9 parts of a poly-3-methylpentane adipate diol with a molecular weight of 2,000, 21.4 parts of an N,N-dimethylaminopropylamine-propylene oxide 2 mole adduct with a molecular weight of 213, and 65.2 parts of IPD had been mixed, the

IPA  
isopropyl  
alcohol

3-5  
10  
15

cont. 10 parts  
100

12, 14, 11, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58, 60, 62, 64, 66, 68, 70, 72, 74, 76, 78, 80, 82, 84, 86, 88, 90, 92, 94, 96, 98, 100

contents were reacted at 100°C over a [n 8]-hour period, and as a result, a urethane prepolymer with an NCO content (%) of 2.9 was obtained. After 500 parts of MEK had subsequently been added, a homogeneous solution was obtained, and subsequently, a solution which had been obtained by solubilizing 15.0 parts of isophorodonediamine and 2.5 parts of di-n-butylamine in 200 parts of <sup>P</sup>IPA was added to the aforementioned MEK urethane prepolymer solution. After the addition had been completed, the temperature was elevated, and the contents were reacted at 50°C over an 8-hour period. The concentration and viscosity of the resulting polyurethane resin solution were 30% and 1,800 cps/20°C, respectively. The total amine value of this resin was 36, and /6 the tertiary amine value of the side chain dialkylamino group was 18 (each based on the polyurethane resin solid content standard). Next, printing ink binder II was prepared by using the resulting resin solution as a binder according to procedures otherwise identical to those in Application Example 1.

[0041]

#### Application Example 3

After 142.2 parts of a poly-ε-caprolactone diol, 64.1 parts of an N,N-dimethylaminopropylamine-propylene oxide 6 mole adduct with a molecular weight of 450, and 171.1 parts of IPD had been mixed, the contents were reacted at 100°C, and as a result, a urethane prepolymer with an NCO content (%) of 3.1 was obtained. After 500 parts of MEK had subsequently been added, a homogeneous solution

was obtained. Subsequently, a solution which had been obtained by solubilizing 20.2 parts of 4,4'-diaminodicyclohexylmethane and 2.2 parts of diethanolamine in 200 parts of IPA was added to the aforementioned MEK urethane prepolymer solution. After the addition had been completed, the temperature was elevated, and the contents were reacted at 50°C over an 8-hour period. The concentration and viscosity of the resulting polyurethane resin solution were 30% and 2,500 cps/20°C, respectively. The total amine value of this resin was 52, and the tertiary amine value of the side chain dialkylamino group was 26 (each based on the polyurethane resin solid content standard). Next, printing ink binder III was prepared by using the resulting resin solution as a binder according to procedures otherwise identical to those in Application Example 1.

[0042]

#### Comparative Example 1

After 228.7 parts of a polybutylene adipate diol with a molecular weight of 2,000 and 50.8 parts of IPD had been mixed, the contents were reacted at 100°C over an 8-hour period, and as a result, a urethane prepolymer with an NCO content (%) of 3.40 was obtained. After 500 parts of MEK had subsequently been added, a homogeneous solution was obtained. Subsequently, a solution which had been obtained by solubilizing 17.5 parts of isophoronediamine and 2.5 parts of diethanolamine in 200 parts of IPA was added to the aforementioned MEK urethane prepolymer solution. After the

addition had been completed, the temperature was elevated, and the contents were reacted at 50°C over an 8-hour period. The concentration and viscosity of the resulting polyurethane resin solution were 30% and 800 cps/20°C, respectively. The total amine value was 0. Next, printing ink binder IV was prepared by using the resulting resin solution as a binder according to procedures otherwise identical to those in Application Example 1.

[0043]

#### Comparative Example 2

After 22[4.1] parts of a polybutylene adipate diol with a molecular weight of 2,000 and 50.6 parts of IPDI had been mixed, the contents were reacted at 100°C over an 8-hour period, and as a result, a urethane prepolymer with an NCO content (%) of 3.4 was obtained. After 500 parts of MEK had subsequently been added, a homogeneous solution was obtained. The aforementioned MEK urethane prepolymer solution was dripped into a solution which had been obtained by solubilizing 21.3 parts of isophoronediamine into 200 parts of IPA. After the addition had been completed, the temperature was elevated, and the contents were reacted at 50°C over an 8-hour period. The concentration and viscosity of the polyurethane resin solution, which possessed amino groups at polymer terminals, were 30% and 900 cps/20°C, respectively. The total amine value of this resin was 4.3 (polyurethane resin solid content standard). Next, printing ink binder V was prepared by using the resulting resin solution as a binder according to

procedures otherwise identical to those in Application Example 1.

[0044]

### Comparative Example 3

After 1[78.1] parts of a polybutylene adipate diol with a molecular weight of 2,000, 20.6 parts of N-methyldiethanolamine, and [86.1] parts of IPDI had been mixed, the contents were reacted at 100°C over a [5]-hour period, and as a result, a urethane prepolymer with an NCO (%) content of [8.9] was obtained. After 500 parts of MEK had subsequently been added, a homogeneous solution was obtained. Subsequently, a solution which had been obtained by solubilizing [19.9] parts of isophoronediamine and 3.3 parts of di-n-butylamine in 200 parts of IPA was added to the aforementioned MEK urethane prepolymer solution. After the addition had been completed, the temperature was elevated, and the contents were reacted at 50°C over an 8-hour period. The concentration and viscosity of the resulting polyurethane resin solution were 30% and 1,100 cps/20°C, respectively. The total amine value of this resin was 32 (based on the polyurethane resin solid content standard). Next, printing ink binder VI was prepared by using the resulting resin solution as a binder according to procedures otherwise identical to those in Application Example 1.

[0045]

Application Examples 4 through 6 and Comparative Examples 4 through

6



(Types of amino groups and measurements of amine values): The types of the amino groups of the polyurethane resins employed in printing inks I through VI, which had been obtained in Application Examples 1 through 3 and Comparative Examples 1 through 3 explained above, respectively, and corresponding measurement data are shown in Table I.

Table I

/7

表-1

ポリウレタン樹脂のアミノ基の分類 (1)

項 目 (2)	分類例 4 5 (3) 6	比較例 4 5 (4) 6
印刷インキ (5)	I II III	IV V VI
分子鎖内アミノ基 アミン値 (7)	21 21 21 10 10 20	- - - 0 0 0
分子末端アミノ基 アミン値 (8) (9)	21 21 21 10 10 20	- 21 21 0 4.2 20
全アミン値 (10)	20 20 22	0 4.2 20

(\*) 印等はそれぞれ: (3) 例アミノ基、(4) 例アミノ基を示す。  
アミン値はポリウレタン樹脂固形分標準値を示す。

[(1): Types of the amino groups of polyurethane resins; (2): Categories; (3): Application Example; (4): Comparative Example; (5): Printing ink; (6): Molecule side-chain amino group; (7): Amine value; (8): Molecule terminal amino group; (9): Amine value; (10): Total amine value; (\*): The notations signify the following: ?? : ?? amino group; ?? : Terminal amino group; the amine value is based on the polyurethane resin solid content standard]

[0047]

Application Examples 7 through 9 and Comparative Examples 7 through 9

(Performance test): The ink stabilities of printing inks I through VI, which had been obtained in Application Examples 1 through 3 and Comparative Examples 1 through 3 explained above, respectively, were tested according to the following test procedures.

[0048]

(a) Ink stability

The ink viscosity was measured by using a BL-type viscometer (manufactured by Tokyo Seiki Co.). After 100 parts of each ink, 2 parts of Coronate HL (polyisocyanate curing agent manufactured by Nippori Co.), and 10 parts of ceramic balls had been charged into a container with a content volume of 200 mL, the contents were kneaded by using a paint conditioner and then preserved at 40°C for 1 day. subsequently, the ink viscosity and fluidity were observed. The results are summarized in Table II.

[0049]

A surface-treated polypropylene film (abbreviated as "OPP"), polyester film (abbreviated as "PET"), or a nylon film (abbreviated as "NY") was printed with each of printing inks I through IV by using a bar coater. The resulting printed matters underwent the performance tests shown below. The results are summarized in Table III.

[0050]

(2) Adhesive strength

After Nichiban Cello Tape (width: 12 mm) had been pasted on the printed surface, one end of said Nichiban Cello Tape was quickly peeled at an angle perpendicular to the printed surface, and the printed surface state was observed.

(3) Antitackiness

After a printed surface and a non-printed surface had been laminated, a load of 1.0 kg/cm<sup>2</sup> was impressed at a temperature of 40°C and at a humidity of 60%RH. Said load was removed 24 hours later, and the surface state was observed.

(4) Oil resistance

Each printed matter was immersed in rapeseed oil at 25°C over a 24-hour period, and subsequently, the surface state was observed.

(5) Water resistance

After each printed matter had been immersed in water at 25°C, the surface state was observed.

(6) Heat resistance

After a printed surface and an aluminum foil had been laminated, the resulting structure was heat-sealed by using a heat sealer at [8]0°C and 1 kg/cm<sup>2</sup> for 1 sec., and after it had been peeled, the surface state was observed.

(7) Laminatability

After a urethane adhesive had been coated on each printed matter, a polyethylene film was pressed and adhered, and after the resulting sample had been left unattended at 40°C over a 24-hour period, it was cut into a width of 15 mm, and the 90° peeling strength was measured by using a peeling strength tester (manufactured by Yasuda Seiki Co.).

(8) Pigment dispersibility

The printing ink was measured by using a particle size analyzer. The test results were judged according to the following criteria: ◎: Extremely favorable; ○: Favorable; △: Somewhat inferior; x: Inferior.

Table II

## 表-2

## ① 各インキの安定性試験結果

項 目 ②		実 施 例 7 ③ 8 9			比 較 例 7. ④ 8 9		
印刷インキ⑤		I	II	III	IV	V	VI
インキ ⑥ 作成時	粘 度 ⑧	1	1	2	1	1	1
	流動性 ⑨	○	○	○	○	○	○
硬化剤 ⑦ 添加後	粘 度 ⑧	1	1	2	1	20	1
	流動性 ⑨	○	○	○	○	×	○

(※) 粘度測定単位: Ps/20℃

[(1): Stability test results on each ink; (2): Categories; (3): Application Example; (4): Comparative Example; (5): Printing ink; (6): During the ink preparation (7): After the addition of the curing agent; (8): Viscosity; (8): Fluidity; (\*): Viscosity measured unit: Ps/20°C]

Table III

表-3

① 各インキの印刷試験結果

項 目 ②		実 例 ③ 7 3 0			比 較 例 ④ 7 3 9		
⑤ 印刷インキ		I	II	III	IV	V	VI
⑥ 接着性	PET	○	○	○	○	○	○
	NY	○	○	○	○	○	○
	OPP	○	○	○	×	○	×
⑦ 剥離性	PET	○	○	○	○	○	○
	NY	○	○	○	○	○	○
⑧ 耐油性	PET	○	○	○	○	○	○
⑨ 耐水性	PET	○	○	○	○	○	○
⑩ 耐熱性	PET	○	○	○	○	○	○
⑪ 層間剥離性	PET	○	○	○	△	○	○
⑫ 顔料分散性		○	○	○	△	○	○

[(1): Printing test results on each ink; (2): Categories; (3): Application Example; (4): Comparative Example; (5): Printing ink; (6): Adhesive strength; (7): Antitackiness; (8): Oil resistance; (9): Water resistance; (10): Heat resistance; (11): Laminatability; (12): Pigment dispersibility]

[0053]

(Effects of the invention)

The following effects are achieved by using the binder of the present invention: (1) an excellent adhesive strength can be /9 achieved with a polyolefin film (e.g., polypropylene film, polyethylene film, etc.), and existing problems have been significantly alleviated; moreover, the adhesive strengths with polyester films and nylon films are also favorable; (2) in a case where it is used for a double-liquid ink, it provides an ink binder with an excellent viscosity stability, and existing problems are solved; (3) printed matters obtained by printing printing inks which contain the binder of the present invention exhibit extremely favorable performances (e.g., oil resistance, water resistance, heat resistance, laminatability, pigment dispersibility, etc.). Based on the foregoing effects, the binder of the present invention is suitable for inks (especially special gravure inks, etc. printed on various plastic films such as polyester films, nylon films, polypropylene films, etc.).